

# Decamethylzirconocene-Chalcogenide-Hydride Complexes

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Stoichiometric reaction of  $[(C_5Me_5)_2ZrH_3]Li$  (**1**) with diphenylphosphine sulfide or selenide yields the bimetallic species  $[(C_5Me_5)_2ZrH]_2(\mu-E)$  ( $E = S$  **2**,  $Se$  **3**). These reactions are proposed to proceed via an intermediate of the form  $[(C_5Me_5)_2ZrH_2(EPPH_2)]^-$  with concurrent loss of dihydrogen. Subsequent  $\beta$ -elimination of  $Ph_2PH$  affords **2** and **3** via dimerization and loss of  $Li_2E$ . The initial synthetic strategy to trap an anionic intermediate involved treatment of **1** with diphenylphosphine oxide. This approach failed, affording instead the tetrameric species  $[Ph_2POLi(THF)]_4$  (**4**) and  $Cp^*_2ZrH_2$ . An alternative, successful approach to an oxide anion involved the reaction of **1** with  $Me_3NO$ . The resulting species  $[(C_5Me_5)_2ZrH(OLi(THF))]_2$  (**5**) was isolated, and the species **2–5** have been structurally characterized. These results are presented and the implications discussed.

## Introduction

Early metal complexes containing multiply bonded ligands have drawn much attention. Among the recent highlights are a number of synthetic, structural, and reactivity studies of terminal chalcogenide ( $M = E$ ,  $E = O, S, Se, Te$ ),<sup>1–12</sup> imide, phosphinidene, and arsinidene ( $M = ER$ ,  $E = N, P, As$ ) species.<sup>13–35</sup> Concurrent

with these works, interest in transition metal hydride chemistry has led to the characterization of a variety of monomeric and dimeric early metal polyhydrides.<sup>36–45</sup> Chemistry at the interface of these two areas has only begun to emerge. Bergman and co-workers<sup>9</sup> demonstrated the direct conversion of a terminal Ti-sulfide  $Cp^*_2Ti(S)py$  to the hydride species  $Cp^*_2TiH(SH)$  via the addition of  $H_2$ , while Andersen et al.<sup>46</sup> have very recently described reactions of the Ti(III) hydride  $Cp^*_2Ti(\mu-H)_2Li(tmed)$  with water to give the oxide anion

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Table 1. Crystallographic Parameters<sup>a</sup>

	2	3	4	5
formula	C <sub>40</sub> H <sub>65</sub> SZr <sub>2</sub>	C <sub>40</sub> H <sub>65</sub> SeZr <sub>2</sub>	C <sub>32</sub> H <sub>36</sub> Li <sub>2</sub> O <sub>4</sub> P <sub>2</sub>	C <sub>26</sub> H <sub>42</sub> LiO <sub>2</sub> Zr
fw	757.43	807.32	560.43	492.76
a, Å	14.5600(1)	20.809(3)	11.472(4)	16.4569(5)
b, Å	14.5600(1)	20.8648(14)	13.430(3)	17.3545(5)
c, Å	19.3845(3)	19.239(2)	22.581(5)	19.1495(3)
α, deg			91.76(3)	
β, deg			92.14(3)	
γ, deg			114.56(2)	
V(Å <sup>3</sup> )	4109.39(7)	8353(2)	3158.0(14)	5469.1(2)
space group	P4 <sub>2</sub> 1c	Ccc2	P1	Pbca
d(calc), g cm <sup>-3</sup>	1.224	1.284	1.179	1.197
Z	4	8	2	8
μ, cm <sup>-1</sup>	0.581	1.394	0.170	0.421
no. of data collected	26560	4611	10475	16384
no. of data used	2308	4072	10467	2932
no. of variables	198	389	721	224
R (%)	0.0620	0.0602	0.0492	0.1045
R <sub>w</sub> (%)	0.0640	0.1854	0.1312	0.2305
goodness of fit	2.370	1.726	0.935	1.229

<sup>a</sup> All data collected at 24 °C with Mo Kα radiation (λ = 0.71069 Å), R = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>|, R<sub>w</sub> = [Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)]/Σ[w(F<sub>o</sub><sup>2</sup>)]<sup>0.5</sup>.

[Cp\*<sub>2</sub>TiOLi(THF)]<sub>2</sub>. In this article, we have investigated the chemistry of the trihydride complex [Cp\*<sub>2</sub>ZrH<sub>3</sub>]<sup>-</sup> (**1**)<sup>38</sup> with the secondary phosphine chalcogenides (Ph<sub>2</sub>P(E)H, E = O, S, Se). In the case of the sulfide and selenide, E–P bond cleavage affords dimeric Zr-chalcogenide hydride complexes. While only deprotonation occurs for the phosphine oxide, an oxide-hydride anionic species has been isolated via an alternative synthetic strategy. This latter species is a model for the intermediate en route to the Zr–S(Se) hydride dimers. It is also noteworthy that this species is a rare example of an anionic early metal organometallic complex.<sup>38,46–48</sup>

## Experimental Section

**General Data.** All preparations were done under an atmosphere of dry, O<sub>2</sub>-free N<sub>2</sub> employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubb's type column system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance-300 and 500 operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe<sub>4</sub>. <sup>31</sup>P NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H<sub>3</sub>PO<sub>4</sub>. Galbraith Laboratories Inc. (Knoxville, TN) or Schwarzkopf Laboratories (Woodside, NY) performed combustion analyses. The compound [Cp\*<sub>2</sub>ZrH<sub>3</sub>]Li (**1**)<sup>38</sup> was prepared via literature methods.

**Synthesis of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH]<sub>2</sub>(μ-S) (**2**) and [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH]<sub>2</sub>(μ-Se) (**3**).** These compounds were prepared in a similar manner employing the appropriate diphenylphosphine chalcogenide. Thus, only one representative preparation is provided. Diphenylphosphine sulfide (17 mg, 0.08 mmol) was dissolved in THF (3 mL) and added to a stirred solution of **1** (30 mg, 0.08 mmol) in THF (3 mL). The reaction mixture turned a bright yellow, instantly, and gas evolution occurred quite vigorously. The reaction mixture was stirred overnight. Solvent was removed from the reaction mixture; the residue was extracted with benzene (3 mL), filtered through Celite, and allowed to stand. This afforded bright yellow crystals (24

mg, 79%). **2:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.74, (s, 30H, Me<sub>5</sub>Cp), 1.85 (s, 30H, Me<sub>5</sub>Cp), 3.23 (s, 2H, ZrH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 11.07 (Me<sub>5</sub>Cp), 12.36 (Me<sub>5</sub>Cp), 129.03 (Me<sub>5</sub>Cp), 129.58 (Me<sub>5</sub>Cp). EA Calcd for C<sub>20</sub>H<sub>32</sub>SZr<sub>2</sub>: C, 63.43; H, 8.25. Found: C, 63.25; H, 8.10. **3:** red/orange crystals (yield: 61%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.08 (s, 30H, Me<sub>5</sub>Cp), 2.06 (s, 30H, Me<sub>5</sub>Cp), 6.25 (s, 2H, ZrH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 11.52 (Me<sub>5</sub>Cp), 13.37 (Me<sub>5</sub>Cp), 130.0 (Me<sub>5</sub>Cp), 131.8 (Me<sub>5</sub>Cp). EA Calcd for C<sub>20</sub>H<sub>32</sub>SeZr<sub>2</sub>: C, 59.73; H, 7.77. Found: C, 59.55; H, 7.62.

**Synthesis of [Ph<sub>2</sub>POLi(THF)]<sub>4</sub> (**4**).** To a stirred solution of **1** (30 mg, 0.08 mmol) in THF (4 mL) was added diphenylphosphine oxide (16 mg, 0.08 mmol). The colorless solution was stirred for 36 h, filtered, and left to grow crystals. After 72 h, large, cubic colorless crystals were isolated from the mother liquor. Yield: 47%. <sup>1</sup>H NMR (THF-d<sub>6</sub>): δ 7.32 (t, |J<sub>H-H</sub>| = 6.5 Hz, 2H), 7.49 (t, |J<sub>H-H</sub>| = 6.5 Hz, 4H), 7.72 (d, |J<sub>H-H</sub>| = 6.5 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>6</sub>): δ 120.6, 128.9, 129.6, 130.2. <sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>6</sub>): δ 103.6. EA Calcd for C<sub>16</sub>H<sub>18</sub>LiO<sub>2</sub>P: C, 68.58; H, 6.47. Found: C, 68.39; H, 6.40.

**Synthesis of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH(OLi(THF))]<sub>2</sub> (**5**).** Trimethylamine N-oxide (10 mg, 0.1 mmol) was dissolved in 2 mL of THF and added to a stirred solution of **1** (40 mg, 0.1 mmol) in 2 mL of THF. The colorless reaction mixture was stirred for 12 h, during which time it became pale yellow. Solvent was removed under dynamic vacuum, leaving a pale canary yellow solid. The crude solid was then dissolved in THF (2 mL) and left to crystallize at -35 °C. Large, rectangular colorless crystals (yield: 86%) formed after 12 h. <sup>1</sup>H NMR (THF-d<sub>6</sub>): δ 1.90 (s, 30H, Me<sub>5</sub>Cp), 4.15 (s, 1H, ZrH). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>6</sub>): δ 11.04 (Me<sub>5</sub>Cp), 13.90 (O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 51.67 (O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 112.70 (Me<sub>5</sub>Cp). EA Calcd for C<sub>24</sub>H<sub>38</sub>LiO<sub>2</sub>Zr: C, 63.47; H, 8.94. Found: C, 63.24; H, 8.88.

**X-ray Data Collection and Reduction.** X-ray quality crystals of **2–5** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O<sub>2</sub>-free environment for each crystal. Diffraction experiments were performed either on a Rigaku AFC6 four-circle or a Siemens SMART System CCD diffractometer. In the latter case the data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° < 2θ < 45–50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP

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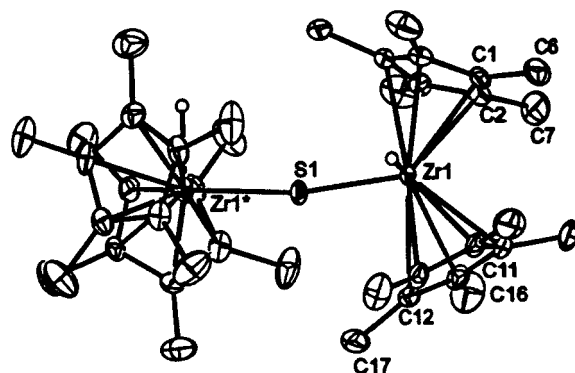
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processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI Challenge mainframe computer with remote X-terminals or a PC employing X-emulation.

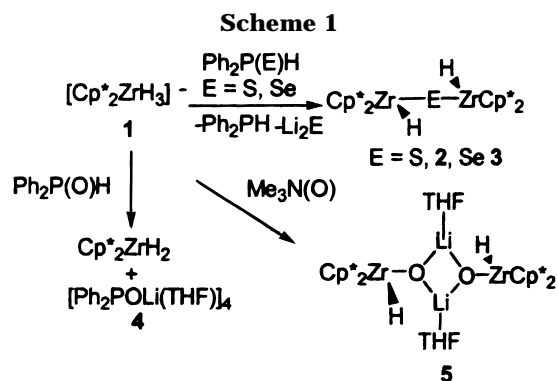
**Structure Solution and Refinement.** Non-hydrogen atomic scattering factors were taken from the literature tabulations.<sup>49,50</sup> The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on  $F$ , minimizing the function  $w(|F_o| - |F_c|)^2$ , where the weight  $w$  is defined as  $4F_o^2/2\sigma(F_o^2)$  and  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. For chiral space groups, the correct enantiomorph was confirmed by data inversion and refinement. The final values of refinement parameters are given in Table 1. In the case of **5** one of the pentamethylcyclopentadienyl ligands as well as the THF coordinated to lithium was disordered and modeled accordingly. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

## Results and Discussion

Stoichiometric reaction of  $[(C_5Me_5)_2ZrH_3]Li$  (**1**) with diphenylphosphine sulfide in THF was evidenced by the vigorous evolution of gas and a concurrent color change to bright yellow. Following stirring for 12 h and solvent concentration, yellow crystals of **2** were isolated in 79% yield.  $^1H$  NMR data revealed the presence of two pentamethylcyclopentadienyl environments and resonance at 3.23 ppm attributable to a Zr-hydride. The formulation of **2** was determined crystallographically to be the 2-fold symmetric species  $[(C_5Me_5)_2ZrH]_2(\mu-S)$  (Figure 1). In this molecule a single sulfur atom bridges two decamethylzirconocene fragments. The Zr–S distance of 2.4432(7) Å in **2** suggests some degree of Zr–S  $\pi$ -bonding, as this is shorter than that seen in  $[Cp_2Zr(\mu-S)]_2$  (2.480(2) Å)<sup>51</sup> and  $(C_5Me_5)_2Zr(S_3)$  (2.521(1) Å)<sup>7</sup> but longer than the terminal Zr=S distance of 2.316(1) Å in  $(C_5Me_5)_2Zr=S(py-t-Bu)_2$  and 2.334(2) Å in  $(C_5Me_4Et)_2Zr=S(py)$ .<sup>6</sup> The bridging sulfur gives rise to a Zr–S–Zr' vector which approaches linearity (168.4(1)°), while the two decamethylzirconocene moieties are orthogonal to each other. The disposition of the linked decamethylmetallocene units in **2** is structurally reminiscent of the mixed valent phosphorus-bridged species  $[(C_5Me_5)_2Zr]_2(\mu-P)$ <sup>52</sup> and the Sm species  $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$  described by Evans et al.<sup>53</sup> The hydride-



**Figure 1.** ORTEP drawings of **2**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Zr(1)–S(1) 2.4432(7) Å; Zr(1)–S(1)–Zr(1') 168.4(1)°.



hydrogen atoms of **2** were refined, revealing a Zr–H distance of 1.86 Å and a S–Zr–H angle of 97.3°. The X-ray data show that the 2-fold symmetry of **2** generates inequivalent  $(C_5Me_5)$  ligands. This feature is maintained in solution, as evidenced by the NMR data, which are consistent with restricted rotation about the Zr–S bonds.

The analogous reaction of **1** with diphenylphosphine selenide proceeds in a similar manner, affording orange/red crystals of compound **3** formulated as  $[(C_5Me_5)_2ZrH]_2(\mu-Se)$  (Scheme 1). Crystallographic data for **3** (Figure 2) confirmed that this species is structurally similar to **2** with an approximately linear (167.24(11)°, 165.76(11)°) Se bridge between two Zr atoms. Two independent halves of the two dimers in which a selenium atom bridges the two decamethylzirconocene fragments occupy the asymmetric unit. The Zr–Se distances are 2.5587(8) and 2.5605(8) Å in **3**. In a manner similar to **2**, these distances are longer than Zr=Se formal double bonds (2.480(1) Å)<sup>6</sup> and shorter than Zr–Se single bonds (2.653(3) Å).<sup>7</sup>

The path of these reactions (Scheme 2) is thought to proceed via initial reaction of diphenylphosphine sulfide (selenide) with **1** affording  $[(C_5Me_5)_2ZrH_2(EPPH_2)]^-$  with concurrent loss of dihydrogen. The proposition of this intermediate is supported in part by our previous characterization of the structurally related complexes  $Cp_2Ti(SPR)_2$ .<sup>54</sup> Subsequent  $\beta$ -elimination of  $Ph_2PH$  from  $[(C_5Me_5)_2ZrH_2(EPPH_2)]^-$  is proposed to yield a

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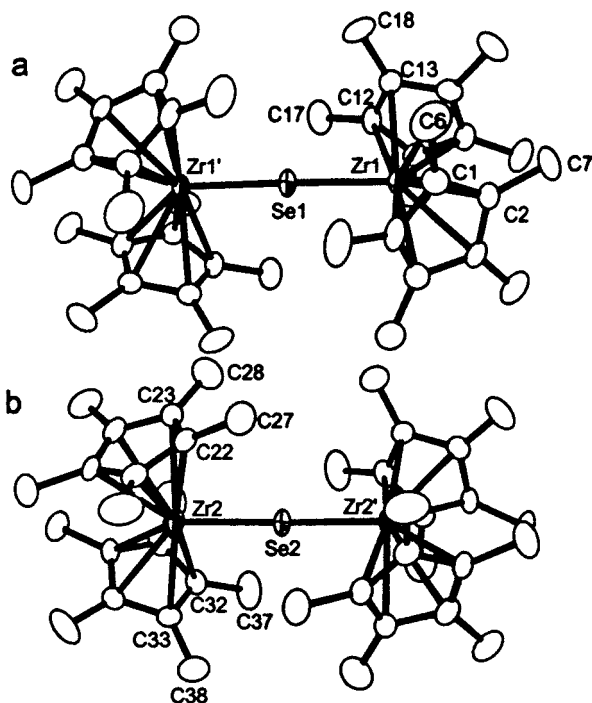
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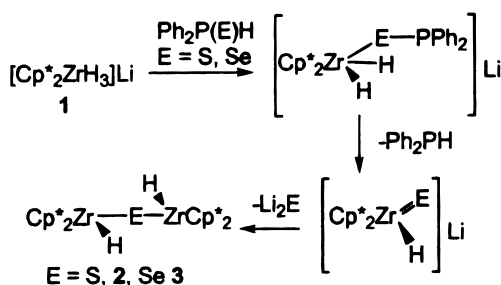
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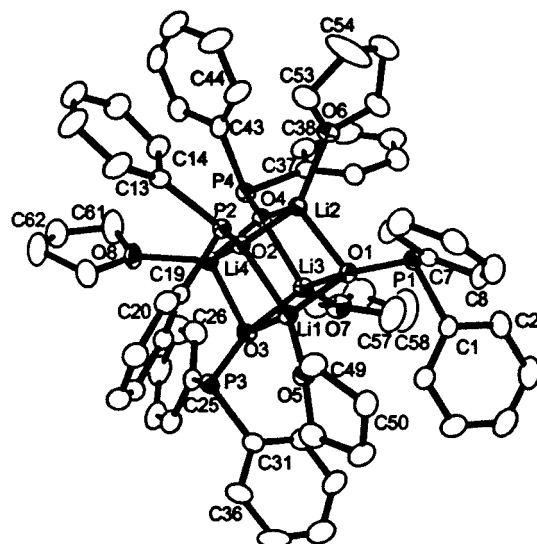
**Figure 2.** ORTEP drawings of the two independent molecules of **3**, a and b. 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Zr(1)–Se(1) 2.5587(8) Å; Zr(2)–Se(2) 2.5606(8) Å; Zr(1)–Se(1)–Zr(1) 167.24(11)°; Zr(2)–Se(2)–Zr(2) 165.76(11)°.

#### Scheme 2



terminal chalcogenide-hydride intermediate species  $[(C_5Me_5)_2ZrH(E)]^-$ , which affords **2** and **3** via dimerization and loss of  $Li_2E$ . While this path is supported by the observation of  $Ph_2PH$  via  $^{31}P$  NMR spectroscopy in reaction mixtures yielding **2** and **3**, attempts to intercept a terminal sulfide or selenide-hydride intermediate have proved unsuccessful to date. Given the oxophilicity of Zr, the analogous oxide anion was targeted.

The initial synthetic strategy involved treatment of **1** with diphenylphosphine oxide. In contrast to the above reactions, no phosphine was liberated and O–P bond cleavage was not observed. Rather, only protonolysis of the phosphine oxide occurred, yielding a crystalline solid **4** and the neutral metallocene dihydride  $(C_5Me_5)_2ZrH_2$ . X-ray crystallography confirmed that **4** is the tetrameric species  $[Ph_2POLi(THF)]_4$  (Figure 3). The Li atoms and the phosphine oxide O atoms alternate in the central  $Li_4O_4$  core. The  $Ph_2P$  fragments surround the core with average P–O distances of 1.586(3) Å. THF molecules complete the coordination spheres of each of the lithium atoms with Li–O distances of 1.952(4)–1.986(5) Å. The geometry about the  $Li_4O_4$  core of **4** is pseudo-cubic (Figure 4) with dimensions approximately equal to the



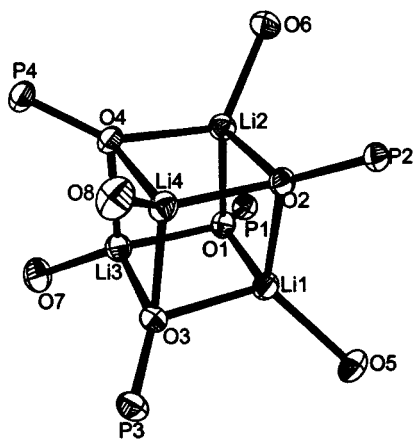
**Figure 3.** ORTEP drawings of **4**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. P(1)–O(1) 1.587(2) Å; P(2)–O(2) 1.586(2) Å; P(3)–O(3) 1.588(2) Å; P(4)–O(4) 1.584(2) Å; O(1)–Li(1) 1.986(5) Å; O(1)–Li(3) 1.986(5) Å; O(1)–Li(2) 2.032(4) Å; O(2)–Li(4) 1.964(5) Å; O(2)–Li(2) 1.992(4) Å; O(2)–Li(1) 2.033(4) Å; O(3)–Li(3) 1.972(5) Å; O(3)–Li(1) 2.015(5) Å; O(3)–Li(4) 2.018(5) Å; O(4)–Li(2) 1.944(5) Å; O(4)–Li(4) 2.009(5) Å; O(4)–Li(3) 2.040(5) Å; O(5)–Li(1) 1.953(4) Å; O(6)–Li(2) 1.986(5) Å; O(7)–Li(3) 1.982(5) Å; O(8)–Li(4) 1.952(5) Å; P(1)–O(1)–Li(1) 139.8(2)°; P(1)–O(1)–Li(3) 131.1(2)°; P(1)–O(1)–Li(2) 115.5(2)°; P(2)–O(2)–Li(4) 139.4(2)°; P(2)–O(2)–Li(2) 127.3(2)°; P(2)–O(2)–Li(1) 120.3(2)°; P(3)–O(3)–Li(3) 146.2(2)°; P(3)–O(3)–Li(1) 124.1(2)°; P(3)–O(3)–Li(4) 114.8(2)°; P(4)–O(4)–Li(2) 146.3(2)°; P(4)–O(4)–Li(4) 121.7(2)°; P(4)–O(4)–Li(3) 118.3(2)°; O(5)–Li(1)–O(1) 120.8(2)°; O(5)–Li(1)–O(3) 122.5(2)°; O(1)–Li(1)–O(3) 96.2(2)°; O(5)–Li(1)–O(2) 121.2(2)°; O(1)–Li(1)–O(2) 95.2(2)°; O(3)–Li(1)–O(2) 94.2(2)°; O(4)–Li(2)–O(6) 123.5(2)°; O(4)–Li(2)–O(2) 97.4(2)°; O(6)–Li(2)–O(2) 118.4(2)°; O(4)–Li(2)–O(1) 96.6(2)°; O(6)–Li(2)–O(1) 119.8(2)°; O(2)–Li(2)–O(1) 95.1(2)°; O(3)–Li(3)–O(7) 124.3(2)°; O(3)–Li(3)–O(1) 97.6(2)°; O(7)–Li(3)–O(1) 118.7(3)°; O(3)–Li(3)–O(4) 94.9(2)°; O(7)–Li(3)–O(4) 119.9(2)°; O(1)–Li(3)–O(4) 95.0(2)°; O(8)–Li(4)–O(2) 123.5(2)°; O(8)–Li(4)–O(4) 121.0(2)°; O(2)–Li(4)–O(4) 96.2(2)°; O(8)–Li(4)–O(3) 118.8(2)°; O(2)–Li(4)–O(3) 96.3(2)°; O(4)–Li(4)–O(3) 94.5(2)°; Li(1)–O(1)–Li(3) 83.2(2)°; Li(1)–O(1)–Li(2) 84.5(2)°; Li(3)–O(1)–Li(2) 83.4(2)°; Li(4)–O(2)–Li(2) 83.0(2)°; Li(4)–O(2)–Li(1) 84.9(2)°; Li(2)–O(2)–Li(1) 84.3(2)°; Li(3)–O(3)–Li(1) 82.8(2)°; Li(3)–O(3)–Li(4) 85.6(2)°; Li(1)–O(3)–Li(4) 84.0(2)°; Li(2)–O(4)–Li(4) 83.0(2)°; Li(2)–O(4)–Li(3) 84.2(2)°; Li(4)–O(4)–Li(3) 84.0(2)°.

O–Li distances ranging from 1.944(5) to 2.040(5) Å. The O–Li–O angles about the core are narrowly dispersed between 94.5(2)° and 97.6(2)°, while the Li–O–Li angles vary from 83.0(2)° to 85.6(2)°. Similar tetrameric aggregates have been confirmed crystallographically for the lithium alkoxides, lithium *N*-methylpseudoephedrate<sup>55</sup> and lithium *N*-methylephedrate.<sup>56</sup>

An alternative synthetic route to an oxide-hydride anion was based on a nonprotic oxygen atom transfer reaction. Reaction of **1** with  $Me_3NO$  proceeds, and  $^1H$  NMR data reveal the consumption of the starting

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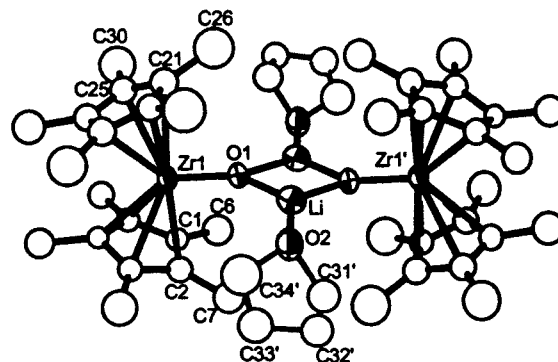


**Figure 4.** ORTEP drawing of the cubane-like core of **4**.

material **1** and the appearance of a new species **5**. This product exhibited a singlet resonance at 4.15 ppm attributable to a single hydride atom, in addition to a single resonance ascribed to the  $(C_5Me_5)$  rings and two resonances corresponding to free and complexed THF. The molecular symmetry implied by the NMR data precluded formulation of **5** as the known oxo-bridged compound  $[(C_5Me_5)_2ZrH]_2(\mu-O)$ .<sup>57</sup> The observation of an infrared absorption at  $765\text{ cm}^{-1}$  was attributed to a terminal Zr-oxide, while the red-shift of this absorption compared to the neutral terminal oxide complexes (e.g.,  $(C_5Me_5)_2Zr=O(py)$ :  $780\text{ cm}^{-1}$ )<sup>8</sup> was consistent with an anionic species. X-ray diffraction confirmed the formulation of **5** as  $[(C_5Me_5)_2ZrH(OLi(THF))]_2$  (Figure 5).

The asymmetric unit is comprised of the anionic metallocene unit containing an oxide ligand, which is associated with a Li cation. Two Li atoms bridge two of these Zr=O fragments (Li–O:  $1.84(3)\text{ \AA}$ ), while molecules of THF complete the coordination spheres of the Li atoms. The geometry about the  $Li_2O_2$  core is very similar to that seen in the related Ti species  $[Cp^*_2TiOLi(THF)]_2$  and thus suggests a structural similarity to the lithium alkoxides as described by Andersen et al.<sup>46</sup> However, the Zr–O distance in **5**,  $1.847(9)\text{ \AA}$ , is only slightly longer than the Zr–O distance in the only terminal Zr-oxide complex known,  $(C_5Me_4Et)_2Zr=O(py)$  ( $1.804(4)\text{ \AA}$ ).<sup>6</sup> This suggests significant Zr–O  $\pi$ -bonding, as the slightly longer Zr–O distance in **5** is consistent with the presence of the formal anionic charge. In the related Ti(III) system, substantial Ti–O  $\pi$ -bonding has also been proposed for  $Cp^*_2TiOLi(THF)]_2$  on the basis of the large  $g_{av}$  observed in the solution EPR spectrum.<sup>46</sup>

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**Figure 5.** ORTEP drawings of **5**, 30% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Only one of the set of positions for the disordered pentamethylcyclopentadienyl ligand and the THF molecules is shown. Zr(1)–O(1)  $1.847(9)\text{ \AA}$ ; O(1)–Li(1)  $1.85(3)\text{ \AA}$ ; O(2)–Li(1)  $1.99(3)\text{ \AA}$ ; Li(1)–Zr(1)  $3.49(3)\text{ \AA}$ ; Li(1)–O(1)–Zr(1)  $138.1(10)^\circ$ ; Li(1)–O(1)–Li(1)'  $78.4(12)^\circ$ ; Zr(1)–O(1)–Li(1)'  $143.0(10)^\circ$ ; O(1)–Li(1)–O(1)'  $101.6(12)^\circ$ ; O(1)–Li(1)–O(2)  $131(2)^\circ$ ; O(1)'–Li(1)–O(2)  $127(2)^\circ$ ; O(1)–Li(1)–Zr(1)  $20.9(5)^\circ$ .

The association of the anion with Li suggests charge buildup on oxygen, consistent with the notion of a significant ionic component in the Zr–O bond of  $(C_5Me_4Et)_2Zr=O(py)$  proposed by Howard and Parkin<sup>6</sup> and supported by the population analysis for M–E interactions described by Ziegler et al.<sup>58</sup> It is this ionic nature that may well allow species **5** to act as a synthon for novel oxo-bridged homo- and hetero-bimetallics. This aspect, as well as the reactivity of **2** and **3**, is currently under study and will be reported in due course.

### Conclusion

In summary, the trihydride species **1** reacts with diphenylphosphine sulfide or selenide, yielding the bimetallic species **2** and **3**. In contrast, reaction of **1** with diphenylphosphine oxide proceeds via acid–base chemistry to give the tetrameric species **4** and  $Cp^*_2ZrH_2$ . The formation of **2** and **3** is proposed to proceed through an anionic intermediate, a view that is supported by the isolation of **5**.

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**Supporting Information Available:** Crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990180P

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